

METAL HYDRIDES AS A SOURCE OF HYDROGEN FUEL

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Hydrogen has the potential of being a cheap and non-polluting fuel which could be used in a variety of energy converters. It is particularly attractive for use in fuel cells, where it is the preferred fuel, but it could also be used in any type of combustion engine, although in the latter case some modification of conventional designs would be required. However, a major problem involved in using hydrogen as a common fuel is the difficulty encountered in storing and transporting it. To store and transport hydrogen as a cryogenic liquid or as a compressed gas for such use does not appear practical either from an economic or a safety standpoint.

Recent studies¹⁻³ on the equilibrium relationships between hydrogen and certain metals and alloys suggest that the reversible metal hydrides formed in these systems may serve as a convenient, safe, and cheap means of storing hydrogen. In this regard the use of magnesium hydride as a source of hydrogen fuel for internal combustion engines has already been discussed.⁴ The object of this paper is to describe how such metal hydrides may be used to supply hydrogen for use as a fuel in an electrochemical cell.

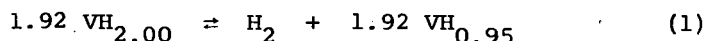
In its most simple form such a storage system consists of a vessel containing a reversible metal hydride of the type described below, a means by which heat may be added to or removed from the system, and a tap for withdrawing or adding hydrogen gas. In operation, as hydrogen is withdrawn from the system, the hydrogen pressure drops below the equilibrium dissociation pressure of the metal hydride which will then dissociate in order to re-establish equilibrium conditions. During the hydrogen evolution step heat must be added to the system since the dissociation reaction is endothermic. Dissociation will continue under these conditions as long as the designated hydride phase exists (it is possible to have more than one hydride phase present in certain systems). In order to regenerate the hydride the procedure is reversed; hydrogen is added to the

system and the hydrogen pressure is maintained above the dissociation pressure. Heat must be removed from the system during this step.

In Table 1 the pertinent properties of three candidate metal hydrides are listed and can be compared to corresponding figures for cryogenic and compressed gas storage. These compounds are vanadium dihydride (VH_2), magnesium nickel hydride (Mg_2NiH_4) and MgH_2 . It is interesting to note that on a volume basis the hydrogen content of the solids is greater than that of liquid hydrogen and much greater than that of compressed hydrogen at 100 atm. pressure and 25°C . We wish to point out that a detailed discussion of the properties and synthesis of these compounds has already been given;¹⁻³ here we shall only discuss these properties briefly and in connection without particular intent.

Vanadium Dihydride - A Low Temperature Hydrogen Reservoir

Vanadium dihydride is capable of supplying hydrogen at a pressure of >1 atm. to a fuel cell at any temperature above $\sim 10^\circ\text{C}$. It has a grey metallic appearance, is very brittle and can easily be ground to a fine powder. It is not pyrophoric, indeed in the presence of air its decomposition is inhibited. It can be synthesized by the direct reaction of hydrogen with the metal or with vanadium monohydride. It will decompose to form vanadium monohydride and hydrogen as follows:³



A plot showing the equilibrium dissociation pressure (P_d) vs composition, expressed as the ratio of H atoms/total metal atoms (H/M), is shown in Fig. 1. Reaction (1) refers to the reaction taking place in the plateau region which lies between the limits $\text{VH}_{0.95}$ - $\text{VH}_{2.00}$. In this region the P_d is essentially constant and not dependent on the solid composition. Above $\text{VH}_{2.00}$ the isotherm does not rise vertically but has a slight slope to the right which is due to the nonstoichiometric character of vanadium dihydride. Below a composition corresponding to $\text{VH}_{0.95}$ the P_d drops precipitously as only the vanadium monohydride phase is present which is quite stable.

The dissociation pressure (P_d) of VH_2 is very sensitive to the type and amount of impurities present in the starting vanadium. Thus, it has been found that the P_d of VH_2 made from commercial grade vanadium (Union Carbide Corp., Materials System Division) was higher by a factor of >2 than that made from high purity vanadium.³ Since a higher P_d is desirable for our purposes we shall specify that the VH_2 used in the systems described here be made from commercial vanadium; the data presented here has been obtained with VH_2 using this as the starting material. Qualitative observation also indicated that these impurities have a catalytic effect, increasing both the rate of decomposition and formation of VH_2 .

A plot of the reciprocal temperature vs the P_d for the composition range $VH_{0.95}$ to $VH_{2.00}$ yields a straight line (Fig. 2) which obeys the equation $\log P_{atm} = \frac{-1989}{T_{oK}} + 7.3795$. From these data the following thermodynamic quantities for reaction (1) can be calculated:

$$\Delta H_{298} = +9.10 \text{ Kcal}$$

$$\Delta S_{298} = +33.76 \text{ eu}$$

$$\Delta F_{298} = -0.96 \text{ Kcal}$$

Thus, the decomposition of VH_2 is endothermic and heat must be supplied. However, at $298^\circ K$ the free energy change is negative and the reaction is spontaneous. Even at a temperature as low as $0^\circ C$ the equilibrium dissociation pressure is slightly above 1 atm. (1.25 atm.). Consequently, VH_2 can supply hydrogen at a usable pressure by extracting heat from the surrounding environment if the ambient temperature is above $0^\circ C$. While this may be convenient in certain circumstances it is probably more efficient to utilize the waste heat of the energy converter to effect decomposition.

An idealized schematic of an integrated H_2 -air fuel cell and a table of compatible metal hydride-fuel cell systems is shown in Fig. 3. As an example of a low temperature system, consider a fuel cell of the type described previously by Bartosh⁵ but with H_2 supplied by the decomposition of VH_2 . The cell was a 500-watt H_2 -air cell operating at $74^\circ C$ with an aqueous KOH electrolyte. Hydrogen originally was supplied by a companion reforming-purification unit which required a low sulfur, hydrocarbon feed. The volume of the reforming unit was 1.4 ft^3 .

weighed 47 lb, including fuel and water, and at maximum cell power the rate of H_2 feed was 0.0632 lb/hr or 14.23 g mole/hr. We may replace the reformer with a reservoir containing VH_2 and at this rate of consumption, 14.45 Kg (31.8 lb) of VH_2 will last 10 hr. The volume of the fuel reservoir required for this amount, assuming a 50% void space, is 5.78 l (0.20 ft³). The amount of energy required to provide the heat of dissociation is 129.5 Kcal/hr (513 Btu/hr). The waste heat generated by the cell, at 55% efficiency, is 351 Kcal/hr (1393 Btu/hr). The only significant difference between the cell described here and that of Bartosh is that we propose to have a circulating electrolyte which is used to transfer the waste heat of the cell to the hydride bed. Considering that the waste heat is in excess by a factor of almost 3 over that required to dissociate VH_2 and the large temperature difference between the hydride bed and the fuel cell, it is quite possible that simpler means of heat transfer would suffice, e.g. locating the hydride bed in an air stream previously used to cool the fuel cell. Thus, the design as shown in Fig. 3 appears quite conservative and allows a considerable degree of flexibility.

As far as start-up procedure is concerned, we would note that the dissociation pressure of VH_2 is high enough to supply hydrogen at the cell operating pressure of 28 psia down to ambient temperature of 7°C. Of course, the bed will tend to cool as the hydride decomposes and the pressure will drop, but the sensible heat of the bed should be sufficient to supply the heat required until some heat is available from the cell. In addition as the bed cools below the ambient temperature some heat will be extracted from the surrounding environment.

When the VH_2 content of the reservoir is exhausted it can be regenerated by supplying H_2 at a pressure of >200 psia at a bed temperature of 25°C. It is necessary to conduct the regeneration reaction at a pressure substantially above the P_d since there is appreciable hysteresis in the system. Further, the rate of regeneration at any fixed temperature is pressure dependent and pressures of 200-300 psia above the P_d are recommended to attain reasonably fast reaction rates. In the latter case qualitative observation suggests that the hydride can be 90% regenerated in about 1 hr, provided sufficient cooling capacity is available to maintain the bed at 25°C.

It is possible to adapt the hydride storage concept to a more conventional scheme also shown in Fig. 3. In this case VH_2 is used to provide a ballast effect in a reformer system. Hydrogen is manufactured from a hydrocarbon fuel and purified in the usual manner by passing it through palladium-silver membrane. The hydrogen may be conducted to the hydride reservoir to regenerate VH_2 , or directly to the fuel cell, or both. Under peak loads the system can be designed so that some VH_2 will decompose to supply the required extra hydrogen. If the fuel cell operation is intermittent, the hydride reservoir may carry most of the load during cell operation and is regenerated when the cell is down. Such an arrangement has several advantages over conventional hydrocarbon reforming-fuel cell systems which are summarized as follows:

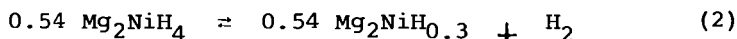
1. The reformer size is determined by the average hydrogen consumption, not peak consumption.
2. The size of the palladium silver diffuser is also determined by the average hydrogen consumption.
3. The reformer can be run continuously and hydrogen stored in the hydride bed for future use.
4. The VH_2 bed can supply H_2 immediately upon start-up.

The actual design of such a system will depend a great deal upon the use pattern envisioned for the fuel cell. However, it can be seen that the incorporation of a relatively small hydride reservoir should result in a practical fuel cell system having a greater degree of flexibility than any previously known.

High Temperature Systems

Both the Mg_2NiH_4 and MgH_2 may be considered in the present context as high temperature systems. They cannot abstract the heat required for decomposition from the environment; rather, such heat must come from the waste heat of the energy converter, provided its operating temperature is high enough, or from some other high temperature heat source. The most efficient arrangement is to use the waste heat of the converter and we will limit our discussion to that particular alternative.

Mg_2NiH_4 is a rust-colored powder having a non-metallic appearance. It is not pyrophoric and it decomposes slowly in water but rapidly in a slightly acidified solution. A pressure composition isotherm for the Mg_2NiH_4 system is shown in Fig. 1. Unlike VH_2 almost all the hydrogen is available except for a small amount which dissolves in the Mg_2Ni decomposition product. The decomposition reaction is as follows:



A plot of the dissociation pressure vs the reciprocal temperature is shown in Fig. 4. It is a straight line and obeys the relationship $\log P_{atm} = -3360/T^{\circ}K + 6.389$. For reaction (2) the following thermodynamic values have been determined²:

$$\Delta H_{2980} = +15.4 \text{ Kcal}$$

$$\Delta F_{298} = +6.7 \text{ Kcal}$$

$$\Delta S_{298} = +29.2 \text{ eu}$$

The reason for including Mg_2NiH_4 in this discussion is that it could be used to supply hydrogen to Bacon type fuel cells operating near $300^{\circ}C$. The high cell temperature would require that the electrolyte be a highly concentrated KOH solution (at least 85 wt % KOH). The advantage of Mg_2NiH_4 over VH_2 in this situation is that it contains 3.3 wt % available hydrogen vs 2.1 wt % for the latter. However, it is only useful in a relatively narrow temperature range from $\sim 275^{\circ}C$ where its P_d is 1.81 atm. to $325^{\circ}C$ at which point the P_d of MgH_2 is 2.8 atm. The latter, of course, contains much more hydrogen on weight basis and for this reason would be the preferred fuel. Unfortunately Bacon type cells operate at temperatures which are too low to utilize the waste heat in order to dissociate MgH_2 . Thus, making the assumption that Bacon cells were available of the same rating and H_2 fuel requirement as the low temperature cell discussed above, the equivalent amount of Mg_2NiH_4 necessary would be 8.56 Kg (18.8 lb) and would require a reservoir volume of 6.66 liters (0.23 ft^3) assuming a 50% void space. The hydride regeneration procedure is similar to that previously described for VH_2 except that the regeneration temperature should be above $250^{\circ}C$ in order to attain an acceptable reaction rate.

For high temperature fuel cells such as those using molten carbonates or solid electrolytes, MgH_2 could be used as the source of hydrogen fuel. However, the preparation of pure MgH_2 by direct reaction with hydrogen is difficult and requires a temperatures of $\sim 400^\circ C$ and ~ 100 atm. pressure.⁴ In addition, the product is quite inert. However, it has been found that if a magnesium alloy containing 5-10 wt % Ni or Cu is used as the starting material the synthesis reaction is greatly accelerated and the product very active.^{1,2} For hydrogen storage purposes, an alloy of 95% Mg and 5% Ni is recommended. Hydrogen will react with this material to form both MgH_2 and Mg_2NiH_4 . Decomposition will take place in two steps; first Mg_2NiH_4 decomposes as shown above in reaction (2), followed by the known reaction:



A pressure composition isotherm for such a system is shown in Fig. 1. The short upper plateau is due to the presence of Mg_2NiH_4 .

A plot of the P_d vs the reciprocal temperature for MgH_2 is shown in Fig. 4. It is a straight line and can be represented by the equation $\log P_{atm} = -4045/T + 7.224$. Assuming Mg_2NiH_4 (or Mg_2Ni) acts purely as a catalyst and that there is no solubility of H_2 in the Mg phase, the following thermodynamic functions have been calculated for reaction (3)²:

$$\Delta H_{298}^{\circ} K = +18.5 \text{ Kcal}$$

$$\Delta F_{298}^{\circ} K = +8.7 \text{ Kcal}$$

$$\Delta S_{298}^{\circ} K = +33 \text{ eu}$$

The equilibrium dissociation pressure of MgH_2 at $325^\circ C$ is 2.85 atm. and this material could be used in any system provided the waste heat could be extracted at that temperature or above. It appears to be quite suitable for high temperature cells using molten carbonate electrolytes which operate above $400^\circ C$. However, since the optimum MgH_2 temperature is about $350^\circ C$ ($P_d = 5.4$ atm.), the fused salt electrolyte cannot be used as a heat transfer medium because this temperature is about $50^\circ C$ below the melting point of the lowest melting eutectic mixture of sodium,

lithium and potassium carbonates. The operation of the metal hydride reservoir at 400°C , where the P_d is 16.4 atm., is not recommended because it is in a temperature and pressure region where the strength of materials may be a problem and leaves no safety margin as far as the molten salt is concerned. Thus a secondary heat transfer medium would have to be used, perhaps a liquid metal (e.g. mercury or sodium), or gas (i.e. air).

The great advantage of MgH_2 is, of course, its high hydrogen content. In this case, in order to power a high temperature cell, similar to the 500-watt cell described above, the total weight of material (91.2% MgH_2 , 8.8% Mg_2NiH_4) required to give the same operating characteristics would be 3.950 Kg (8.69 lb), having a volume (50% void space) of about 5.4 liters (0.19 ft^3). Because of the presence of the ternary hydride, the hydrogen content of the mixture is 7.3 wt % rather than 7.6 wt % as it is in pure MgH_2 . In calculating the volume we made no correction for the probable increase in density resulting from the presence of Mg_2NiH_4 and have assumed the density of the mixture is the same as that of pure MgH_2 , i.e. 1.45 g/cc.

A hydride reservoir containing Mg_2NiH_4 or MgH_2 could also be used to give a ballast effect in a reformer system as described above using VH_2 . The higher hydrogen content of these compounds vs VH_2 is somewhat offset by the higher decomposition temperature required for the former, otherwise the same advantages would accrue as those enumerated above.

Conclusions

We have shown how several reversible metal hydride systems may be used to supply hydrogen to several types of electrochemical fuel cells. In our judgment VH_2 is the preferred material for such use because of its convenience, flexibility and the ease with which it could be integrated with the most advanced fuel cell type, i.e. aqueous, low temperature systems. However, the large hydrogen content of MgH_2 could be a determining factor in certain circumstances where weight may be an over-riding consideration. The ternary hydride Mg_2NiH_4 is of interest primarily because it could be used in conjunction with high temperature Bacon cells.

It is our contention that these compounds have the potential to solve a serious and long-term problem associated

with the development of a practical and economical fuel cell, i.e. the storage and generation of hydrogen. It is also apparent that they could be used in a number of alternative schemes not discussed here, where these properties would constitute an important advantage and improvement.

Acknowledgment

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References

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Table 1

	<u>VH₂</u>	<u>Mg₂NiH₄</u>	<u>MgH₂</u>	<u>H₂ Gas</u>	<u>Liq. H₂</u>
Available Hydrogen Wt %	2.1	3.3	7.6	100	100
Density g/ml	~5	2.57	1.45	7.2×10^{-3}	7×10^{-2}
Available Hydrogen g/ml of Volume	0.105	0.085	0.110	7.2×10^{-3}	7×10^{-2}

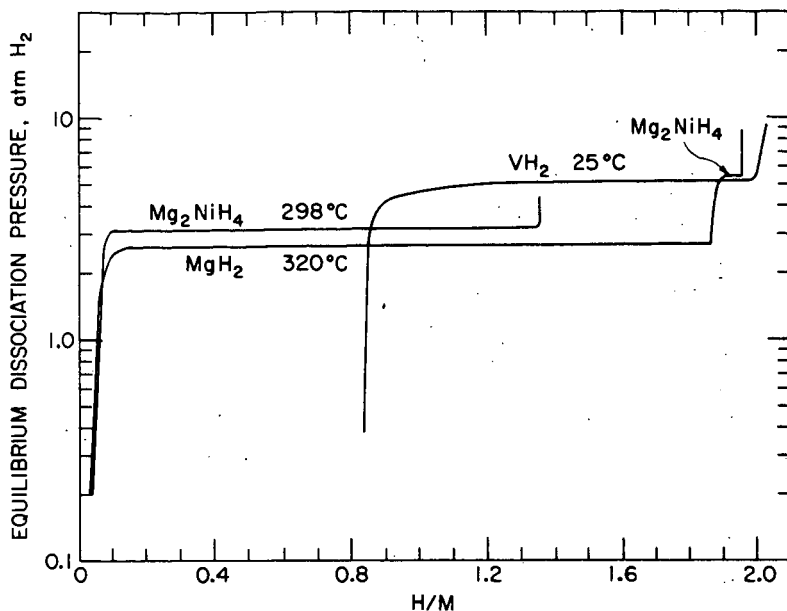


Fig. 1
Pressure-Composition Isotherms
for Systems Indicated.

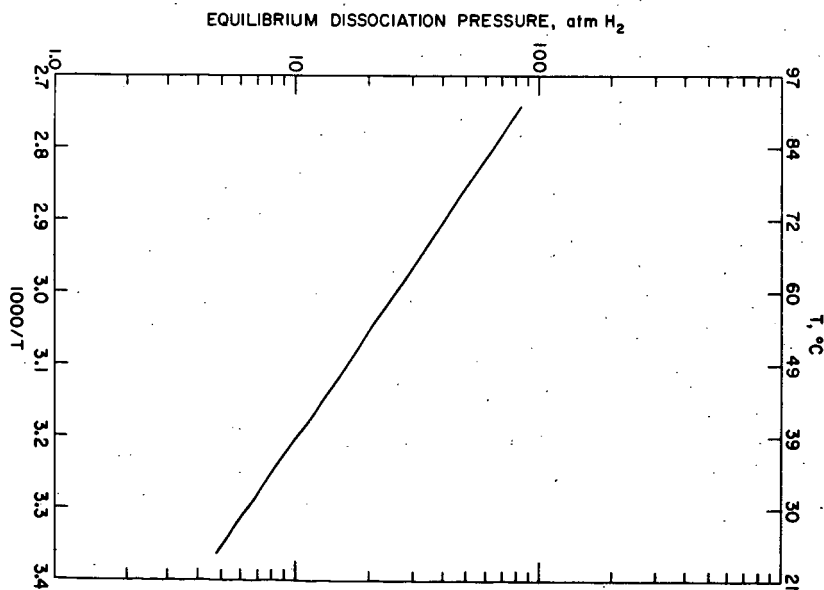
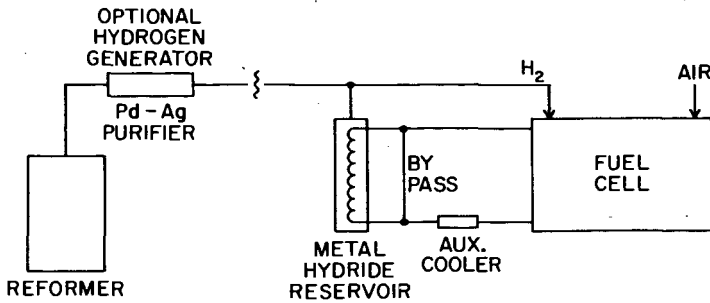


Fig. 2
Equilibrium Dissociation Pressure
of VH_2 vs $1000/T^\circ K$



METAL HYDRIDE	TEMP. °C	EQUIL. PRESS. atm	FUEL CELL	
			TEMP. °C	H ₂ FEED PRESS. atm
VH ₂	25	5	75	2
Mg ₂ NiH ₄	290	2.6	300	"
MgH ₂	340	5	>400	"

Fig. 3
Schematic of Integrated
Metal Hydride - Fuel Cell System

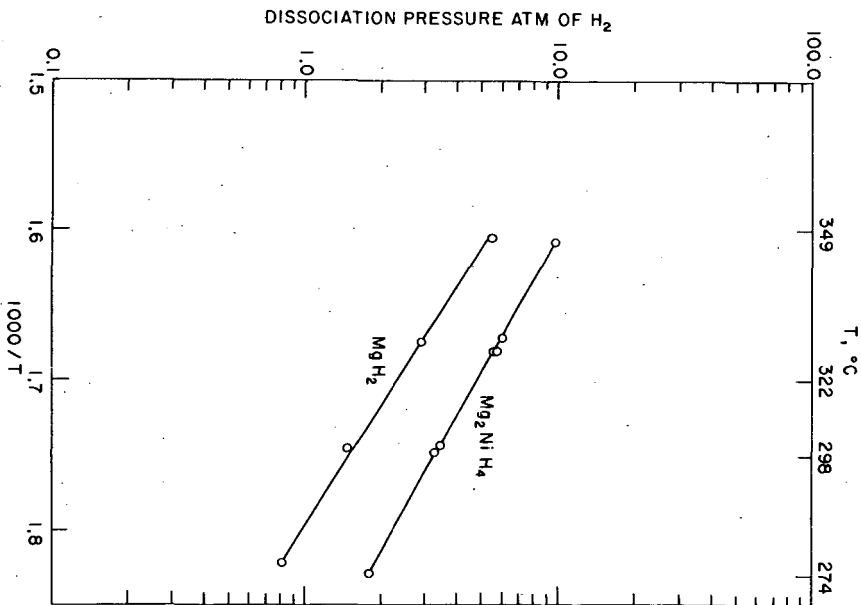


Fig. 4
Dissociation Pressure of
MgH₂ and Mg₂NiH₄ vs 1000/T°K